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(71) Applicant(s)

Everlight Chemical Industrial Corporation
(Incorporated in Taiwan)
6th Floor Chung Ting Building,
No 77 Sec 2 Tun Hua S Road, Taipei,
Taiwan

(72) Inventor(s)

Chuan-hsi Li
Chien-wen Li
Hong-Chang Huang

(74) Agent and/or Address for Service

Barker Brettell
138 Hagley Road, Edgbaston,
BIRMINGHAM, B16 9PW, United Kingdom

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GB 2318798 A	GB 2252335 A
EP 0620116 A2	JP 040183759 A
US 5603756 A	US 4969951 A

(58) Field of Search

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(54) Abstract Title

Ink composition for ink-jet textile printing

(57) An ink composition for ink-jet textile printing comprises (a) at least a reactive dye; (b) water; and (c) at least an organic solvent which is a C₄-C₆ polyhydric alcohol having one or less primary alcohol groups. The reactive dye may be selected from monochlorotriazinyl, sulfatoethylsulfone and vinylsulfone derivative dyes and the C₄-C₆ polyhydric alcohol may include hexylene glycol, 1,2-butanediol, 2,3-butanediol etc. The ink composition may also further include a buffer, a microbicide and a surfactant e.g acetylene glycol. A method of using the ink composition for dyeing and printing of materials containing cellulose fibres such as cotton is also disclosed.

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INK COMPOSITION FOR INK-JET TEXTILE PRINTING

BACKGROUND OF THE INVENTION

1. Field of the Invention

5 The present invention relates to an ink composition for ink-jet textile printing, and particularly to an ink composition for ink-jet textile printing suitable for dyeing and printing of materials containing cellulose fibers.

2. Related Prior Art

10 Textile printing is one of the most popular technologies in the textile industry, since no halftone is necessary cost and processing time can be reduced, even though versatile patterns are desired.

 For textile printing, required ink composition properties are viscosity, stability, surface tension and mobility. Furthermore, the printed fabrics
15 should have high-quality colour strength, fixation, fiber-dye bond stability, and wet fastness.

 In general, the dyes or pigments can be dissolved or dispersed in water or liquid containing water-soluble solvents. Proper surfactants can be added to the ink compositions to modify characteristics thereof.

20 USP 5,603,756 disclosed an ink composition including at least a reactive dye, polyhydric alcohol and water, which further includes a reaction product of the reactive dye with polyhydric alcohol. The polyhydric alcohol used here partially modifies the reactive dyes, however, the colour strength and fixation of the ink composition on fabrics are not satisfying.

25 USP 6,015,454 disclosed another ink composition including at least a reactive dye and 1,2-propylene glycol or N-methyl-2-pyrrolidone, which improved colour strength and fixation. Unfortunately, properties of the ink compositions, such as storage stability, clogging in nozzles and long-term

printing stability are not satisfying.

Accordingly, the present invention provides alternative ink compositions in which specific solvents are added.

5 SUMMARY OF THE INVENTION

An object of the present invention is to provide an ink composition for ink-jet textile printing, which is suitable for dyeing and printing material containing cellulose or other fibers.

Accordingly, the ink composition of the present invention essentially
10 comprises (a) at least a reactive dye, (b) water, and (c) at least an organic solvent which is a C₄-C₆ polyhydric alcohol having one or less primary alcohol groups. The ink composition of the present invention is suitable for ink-jet printers, for example, piezoelectric ink-jet printers and thermobubble ink-jet printers.

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DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

An ink composition for ink-jet textile printing of the present invention essentially comprises (a) at least a reactive dye, (b) water, and (c) at least an organic solvent which is a C₄-C₆ polyhydric alcohol having one or less
20 primary alcohol groups.

For the above mentioned organic solvent, the C₄-C₆ polyhydric alcohol having no primary alcohol group can be 2,3-dimethyl-2,3-butanediol, 2,3-butanediol, 2,4-pentanediol, 2,5-hexanediol, or hexylene glycol; and the C₄-C₆ polyhydric alcohol having one primary alcohol group can be
25 2-methyl-1,2-propanediol, 1,2-butanediol, 1,3-butanediol, 1,2-pentanediol, 1,2-hexanediol, or hexane-1,3,5-triol. Further, the organic solvent can be mixture of these polyhydric alcohols, for example, a mixture of hexylene glycol and 1,3-butanediol.

The above mentioned reactive dye is water-soluble and has a monochlorotriazinyl derivative group, a β -sulfatoethylsulfone derivative group or a vinylsulfone derivative group. Such reactive dyes can be selected from the Color Index, for example, C.I. Reactive Red 3:1, C.I. Reactive Red 23, C.I. Reactive Red 31, C.I. Reactive Red 33, C.I. Reactive Red 24, C.I. Reactive Yellow 2, C.I. Reactive Yellow 18, C.I. Reactive Yellow 80, C.I. Reactive Yellow 95, C.I. Reactive Blue 15, C.I. Reactive Blue 5, C.I. Reactive Blue 49, C.I. Reactive Blue 71, C.I. Reactive Blue 176, C.I. Reactive Orange 12, C.I. Reactive Orange 13, C.I. Reactive Black 8 or C.I. Reactive Black 5.

10 The reactive dyes can be used individually or mixed with each other, or associated with salts of an alkali metal or ammonium thereof. Preferably, the added salt is less than 0.5 wt%. The salts produced during processes and diluents can be removed by membrane separation, ultra-filtration, reverse osmosis, or dialysis.

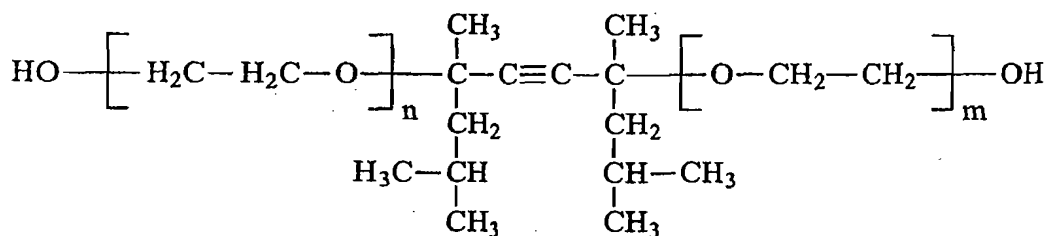
15 In general, the ink composition includes 5-35 wt% of the reactive dye, 35-94.9 wt% of water, and 0.1-30 wt% of the organic solvent, based on the total weight of the ink composition.

Preferably, the ink composition includes 10-30 wt% of the reactive dye, 50-89 wt% of water, and 1-20 wt% of the organic solvent.

20 The organic solvent is usually added at 0.1-30 wt%, preferably between 1-20 wt%, depending on conditions such as wetness of nozzles, stability of printing and storage.

The ink composition of the present invention can further include (d) a non-ionic surfactant, for example, an acetylene glycol derivative of the following formula (II),

25



(II)

wherein the sum of n and m is an integer ranging from 0 to 50, and preferably from 0 to 20. The commercial production includes Surfynol 465, Surfynol 485, Surfynol 420, and Surfynol 104. (Air Products & Chemicals, Inc.). The surfactant is usually added at 0.1-3 wt%, and preferably at 0.1-1 wt%.

The ink composition of the present invention can further include (e) a buffer, whereby the solution can be at pH 4-9, wherein pH 4-8 is preferred, and preferably pH 5-7. The buffer can be acetic acid, acetate, phosphoric acid, phosphate, borax, borate and citrate, for example, acetic acid, sodium acetate, phosphoric acid, sodium phosphate, borax, sodium borate, sodium tetraborate and sodium citrate. The buffer is usually added at 0.1-3 wt%, and preferably at 0.1-1 wt%, based on the total weight of the ink composition.

The ink composition of the present invention can further optionally include (f) a microbicide or an additive, for example, a defoamer. The microbicide is preferably added at 0.01-1 wt%. The additive can be NUOSEPT (Nudex Inc., a division of Huls Americal), UCARCIDE (Union Carbide), VANCIDE (RT Vanderbilt Co.) and PROXEL (ICI Americas). The additive is usually added at 0.01-1 wt% based on the total weight of the ink composition.

The ink composition of the present invention can be prepared by mixing the above components in water according to general procedures.

The ink composition of the present invention can be applied to printing on material containing cellulose fibers such as cotton, hemp,

cellulose, synthetic fibers, and materials containing hydroxyl fibers.

The ink composition of the present invention can be fixed on the fibers by ink-jet printing, and particularly by piezoelectric or thermobubble ink-jet printers.

5 The ink composition of the present invention can provide excellent colour strength, fixation, storage stability, no clogging in nozzles, and stability for long-term printing.

 According to the ink compositions of the present invention, the printed fabrics have high-quality properties such as strong fiber-dye bond stability in
10 both the acidic and the alkaline solution, clear features and good colour strength, and good fastness to light and wet conditions, for example, washing, water, brine, re-dyeing, moisture, chlorinating, rubbing, hot pressing and pleating.

 The following examples are used to illustrate the present invention,
15 but not limited to the scope thereof. In these examples, parts and % are counted by weight, relationship between % weight and % volume is the same as kilograms and liters, and the temperature is in degrees Celsius.

Example 1

20 15.4 parts of C.I. Reactive Yellow 80, 5 parts of hexylene glycol, 0.5 parts of non-ionic surfactant SURFYNOLS 465, 1 part of microbial reagent Proxel xl2, and 78.1 parts of water are mixed well to obtain an ink composition.

25 Examples 2-12 and Comparative Examples 1-6

 Repeat the procedure of Example 1, but the components are added at different amount according to Table 1 and Table 2.

Table 1

Example	Dye (wt%)	Organic Solvent (wt%)	Surfactant (wt%)	Microbial Reagent (wt%)	Water (wt%)
Example 2	C.I. Reactive Yellow 80 (15.4wt%)	1,3-butanediol (5wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (78.1wt%)
Example 3	C.I. Reactive Red 31 (25wt%)	hexylene glycol (5wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (68.5wt%)
Example 4	C.I. Reactive Red 31 (25wt%)	1,3-butanediol (5wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (68.5wt%)
Example 5	C.I. Reactive Blue 15 (25.2wt%)	hexylene glycol (5wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (68.3wt%)
Example 6	C.I. Reactive Blue 15 (25.2wt%)	1,3-butanediol (5wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (68.3wt%)
Example 7	Reactive Black P-2R (14wt%)	hexylene glycol (5wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (79.5wt%)
Example 8	Reactive Black P-2R (14wt%)	1,3-butanediol (5wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (79.5wt%)

Example	Dye (wt%)	Organic Solvent (wt%)	Surfactant (wt%)	Microbial Reagent (wt%)	Water (wt%)
Example 9	Reactive Black P-2R (14wt%)	hexylene glycol (2.5wt%) 1,3-butanediol (2.5wt%)	Surfynols 465 (0.5 wt%)	Proxel xl2 (1 wt%)	Water (79.5wt%)
Example 10	C.I. Reactive Black 5 (14wt%)	hexylene glycol (2.5wt%) 1,3-butanediol (2.5wt%)	Surfynols 465 (0.5 wt%)	Proxel xl2 (1wt%)	Water (79.5wt%)
Example 11	C.I. Reactive Blue 49 (10wt%)	hexylene glycol (15wt%)	--	Proxel xl2 (1wt%)	Water (74wt%)
Example 12	C.I. Reactive Blue 49 (10wt%)	1,3-butanediol (15wt%)	--	Proxel xl2 (1wt%)	Water (74wt%)

Table 2

Comparative Example	Dye (wt%)	Organic Solvent (wt%)	Surfactant (wt%)	Microbial Reagent (wt%)	Water (wt%)
Comparative Example 1	C.I. Reactive Blue 49 (10wt%)	Diethylene Glycol (15wt%)	--	Proxel xl2 (1wt%)	Water (74wt%)
Comparative Example 2	C.I. Reactive Blue 49 (10wt%)	Glycerol (15wt%)	--	Proxel xl2 (1wt%)	Water (74wt%)
Comparative Example 3	C.I. Reactive Blue 49 (10wt%)	Dipropylene glycol (15wt%)	Surfynols 465 (0.5wt%)	Proxel xl2 (1wt%)	Water (74wt%)
Comparative Example 4	C.I. Reactive Blue 49 (10wt%)	Polyethylene glycol 400 (15wt%)	--	Proxel xl2 (1wt%)	Water (74wt%)
Comparative Example 5	C.I. Reactive Blue 49 (10wt%)	1,2,6-hexane triol (15wt%)	--	Proxel xl2 (1wt%)	Water (74wt%)
Comparative Example 6	C.I. Reactive Blue 49 (10wt%)	Triethylene Glycol (15wt%)	--	Proxel xl2 (1wt%)	Water (74wt%)

Comparative Example 7 (Conventional Screen Printing)

100 parts of urea, 10 parts of reduction inhibitor agent, 20 parts of sodium bicarbonate, 60 parts of sodium alginate and 810 parts of warm water, in a sum of 1000 parts, are mixed to obtain an assisting paste. 3 parts of C.I. Reactive Blue 49 is spread on 97 parts of the assisting paste and then rapidly

stirred. A twill half-tone of 45 degrees and 100 meshes goes over a mercerized cotton twill, on which the color paste is then brushed. The fabric is then dried in an oven at 65°C for 5 min. The dried fabric is then steamed with 102-105°C saturated steam in a steamer at normal pressure for 10 min. Finally, the dyed fabric is washed with cold water, boiling water for 10 min, boiling non-ionic detergent for 10 min, and cold water, and then dried.

Comparative Examples 8-11

- 10 Repeat the procedure of Comparative Example 7, but the C.I. Reactive Blue 49 is replaced with the following dyes.

Comparative Example	Dye
Comparative Example 8	C.I. Reactive Yellow 80
Comparative Example 9	C.I. Reactive Red 31
Comparative Example 10	C.I. Reactive Blue 15
Comparative Example 11	Reactive Black P-2R

Printing Test

- 15 1. Pre-treating exhausting fabrics

100 parts of urea, 10 parts of reduction inhibitor agent, 20 parts of sodium bicarbonate, 60 parts of sodium alginate, and 810 parts of warm water, in a sum of 1000 parts, are mixed to obtain the pre-treating solution. 3/1 twill fabrics including natural cellulose fibers, cotton, and regenerated fibers, such as rayon, are used in the test. Before printed, the fabrics are dipped in the pre-treating solution (pick-up 70%) by pressing under a roller and then dried with hot air at 100°C.

2. Printing, Fixing and Post-treating

A thermobubble printer (HP 870C) and a piezoelectric printer (EPSON COLOR 460) are provided for printing. The ink compositions obtained from Examples 1-10 are first applied to the above printers and then printed on the above fabrics. After drying at 50°C for 2 min, these fabrics are brought to fixation in 102-110°C steam for 8-15 min. Finally, the fabrics are washed with 100°C water and water containing detergent in sequence, and then dried.

The test results are listed in Table 3.

Table 3

Example	Bleeding	Stability of Printing	Stability of Storage	
			High Temperature (50°C, 3days)	Low Temperature (-5°C, 3days)
Example 1(Y)	Good	Good	Good	Good
Example 2(Y)	Good	Good	Good	Good
Example 3(M)	Good	Good	Good	Good
Example 4(M)	Good	Good	Good	Good
Example 5(C)	Good	Good	Good	Good
Example 6(C)	Good	Good	Good	Good
Example 7(K)	Good	Good	Good	Good
Example 8(K)	Good	Good	Good	Good
Example 9	Good	Good	Good	Good
Example 10	Good	Good	Good	Good

1. Bleeding: Observing whether the single ink composition printed on one

block leaks outside the edges thereof or two different ink compositions printed on two adjacent blocks leak to each other.

Good: no bleeding

No Good: bleeding

- 5 2. Printing Stability: Observing whether the ink composition gives a continuous flow.

Good: 0-1 nozzles are clogged

Average: 2-3 nozzles are clogged

No Good: 4 or more nozzles are clogged

- 10 3. Low Temperature Storage Stability: Observing for substance separation in the ink compositions (50c.c.) after 3 days of buildup at 0-5°C.

Good: no substance separation

No Good: substance separation

- 15 4. High Temperature Storage Stability: Using a dip dyeing bath, Observing whether the colour strength fade of the ink compositions (50c.c.) after 3 days of storage at 50°C.

Good: 0-5% fading

Average: 5-10% fading

No Good: more than 10% fading

20

In the above printing test, Examples 1, 3, 5 and 7 include a solvent different from Examples 2, 4, 6 and 8; and Examples 9 and 10 include various dyes and solvent mixtures. As shown in Table 3, the ink compositions according to the present invention can provide good properties such as no bleeding, and good stability of printing and storage.

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The ink compositions of Examples 11 and 12 and Comparative Examples 1-6 are printed on fabrics according to the above procedures, and then washed and dried. Fixation rate of these compositions are listed in

Table 4.

The fixation rate is measured according to ABS values of the ink compositions extracted from the fabric before and after fixing, wherein the ABS values are obtained from the UV spectrum.

5

A_0 = ABS of the ink extracted from the fabric (4cm × 5cm) before fixing

A_1 = ABS of the ink extracted from the fabric (4cm × 5cm) after fixing

Fixing rate = $(1 - A_1/A_0)$

10 Table 4

Sample	Organic Solvent	Fixing Rate	Grade
Comparative Example 1	Diethylene Glycol	45%	No Good
Comparative Example 2	Glycerol	40%	No Good
Comparative Example 3	Dipropylene glycol	52%	Worse
Comparative Example 4	Polyethylene glycol 400	30%	No Good
Comparative Example 5	1,2,6-hexanetriol	25%	No Good
Comparative Example 6	Triethylene Glycol	32%	No Good
Comparative Example 7	--	60%	Similar
Example 11	Hexylene glycol	60%	Similar
Example 12	1,3-butanediol	60%	Similar

1. The grades are obtained by comparing with the fixation rate of Comparative Example 7 (conventional screen printing).

Similar: lower by 0-2%

Worse: lower by 2-10%

15

No Good: lower by at least 10%

As shown in Table 4, the ink composition including novel components

Table 6

Example, Comparative Example	Fixation rate	Rubbing Fastness		Washing Fastness	
		Dry	Wet	Nylon	Cotton
Example 1	83%	5	3	5	4-5
Example 2	80%	5	3	5	4-5
Comparative Example 8	75%	5	3	5	4-5
Example 3	58%	4-5	2-3	4-5	4-5
Example 4	59%	4-5	2-3	4-5	4-5
Comparative Example 9	55%	4-5	2-3	4-5	4-5
Example 5	45%	5	2-3	4-5	3-4
Example 6	46%	4-5	2-3	4-5	3-4
Comparative Example 10	37%	5	2-3	5	3-4
Example 7	72%	4-5	2-3	5	4-5
Example 8	69%	4-5	2-3	5	4-5
Comparative Example 11	62%	4-5	2-3	5	4-5

1. The rubbing fastness is measured according to AATCC TEST METHOD 8-1988
- 5 2. The washing fastness is measured according to AATCC TEST METHOD 61-1989 3A

10 In Tables 5 and 6, the ink compositions are sorted into four sets, i.e., Examples 1, 2 and Comparative Example 8, Examples 3, 4 and Comparative Example 9, Examples 5, 6 and Comparative Example 10, and Examples 7, 8 and Comparative Example 11. For each set, the dye is the same and other components are varied. The results indicate that the ink compositions of the present invention can provide higher fixation rate, similar rubbing fastness and

washing fastness when compared with the conventional screen printing.

According to the above Examples and test results, the solvents used in the present invention are particularly suitable for the ink compositions of textile printing, and therefore properties including good colour strength, high
5 fixation rate, good storage stability, no colgging in nozzles, and stable long-term printing can be achieved. Though the solvents used in the present invention have been mentioned in USP 5,603,756, the latter has different purposes and applications, i.e., paper printing. More important, not all solvents mentioned in USP 5,603,756 are suitable for textile printing. Table
10 4 shows that some of them are used in Comparative Examples 1-6 having poor fixation rate.

From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the scope thereof, can make various changes and modifications of the
15 invention to adapt it to various usages and conditions. Thus, other embodiments are also within the claims.

WHAT IS CLAIMED IS:

1. An ink composition for ink-jet textile printing, comprising
(a) at least a reactive dye;
5 (b) water; and
(c) at least an organic solvent which is a C₄-C₆ polyhydric alcohol having one or less primary alcohol groups.
2. The ink composition of claim 1, wherein said organic solvent is a C₄-C₆ polyhydric alcohol having no primary alcohol groups.
- 10 3. The ink composition of claim 2, wherein said C₄-C₆ polyhydric alcohol having no primary alcohol groups is selected from the group consisting of 2,3-dimethyl-2,3-butanediol, 2,3-butanediol, 2,4-pentanediol, 2,5-hexanediol and hexylene glycol.
4. The ink composition of claim 1, wherein said organic
15 solvent is a C₄-C₆ polyhydric alcohol having one primary alcohol group.
5. The ink composition of claim 4, wherein said C₄-C₆ polyhydric alcohol having one primary alcohol group is selected from the group consisting of 2-methyl-1,2-propanediol, 1,2-butanediol, 1,3-butanediol, 1,2-pentanediol, 1,2-hexanediol and hexane-1,3,5-triol.
- 20 6. The ink composition of claim 1, wherein said C₄-C₆ polyhydric alcohol having no primary alcohol groups is hexylene glycol, and said C₄-C₆ polyhydric alcohol having one primary alcohol group is 1,3-butanediol.
7. The ink composition according to any preceding claim,
25 wherein said reactive dye is selected from the group consisting of monochlorotriazinyl, β -sulfatoethylsulfone and vinylsulfone derivative dyes.
8. The ink composition of claim 7, wherein said reactive dye is monochlorotriazinyl derivative dyes.

9. The ink composition of claim 7, wherein said reactive dye is selected from the group consisting of β -sulfatoethylsulfone and vinylsulfone derivative dyes.

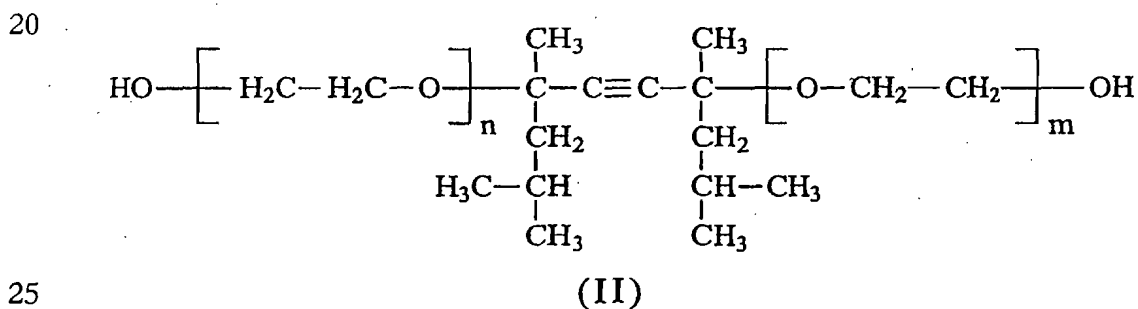
10. The ink composition according to any of claims 1 to 6, wherein said reactive dye is selected from the group consisting of C.I. Reactive Red 3:1, C.I. Reactive Red 23, C.I. Reactive Red 31, C.I. Reactive Red 24, C.I. Reactive Yellow 80, C.I. Reactive Yellow 95, C.I. Reactive Blue 15, C.I. Reactive Blue 49, C.I. Reactive Blue 176, C.I. Reactive Orange 12, C.I. Reactive Black 8, and C.I. Reactive Black 5.

11. The ink composition according to any preceding claim, wherein said reactive dye is 5-35 wt%, said water is 35-94.9 wt%, and said organic solvent is 0.1-30 wt%.

12. The ink composition of claim 11, wherein said reactive dye is 10-30 wt%, said water is 50-89 wt%, and said organic solvent is 1-20 wt%.

13. The ink composition according to any preceding claim, which further comprises (d) a non-ionic surfactant.

14. The ink composition of claim 13, wherein said non-ionic surfactant is an acetylene glycol derivative of the following formula (II),



wherein the sum of n and m is an integer ranging from 0 to 50.

15. The ink composition of claim 14, wherein the sum of n and m is an integer ranging from 0 to 20.

16. The ink composition of claim 13, or claim 14, wherein said non-ionic surfactant is 0.1-3 wt%.

17. The ink composition of any preceding claim, which further comprises (e) a buffer.
18. The ink composition of claim 17, wherein said buffer is 0.1-3 wt%.
- 5 19. The ink composition of any preceding claim, which further comprises (f) a microbicide.
20. The ink composition of claim 19, wherein said microbicide is 0.01-1 wt%.
- 10 21. A method for ink-jet printing on material containing cellulose fibers, which comprises using an ink composition of any preceding claim to process said material containing cellulose fibers.
22. The method of claim 21, wherein said material containing cellulose fibers is cotton.
- 15 23. An ink composition for ink-jet textile printing substantially as described herein.
24. A method for inkjet printing on material containing cellulose fibers substantially as described herein.



INVESTOR IN PEOPLE

Application No: GB 0304598.6
Claims searched: 1-24

Examiner: Dr Jonathan Corden
Date of search: 9 July 2003

Patents Act 1977 : Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance	
X, Y	X: 1-13, 17, 21, 22 Y: 14	US 5603756 A	(CANON) see col 1 lines 12-22, col 3 lines 4-30, col 4 line 46 to col 5 line 7 and col 5 line 45 to col 6 line 17
X, Y	X: 1-13, 17, 21, 22 Y: 14	EP 0620116 A2	(CANON) see page 3 lines 13-54 and page 4 line 13 to page 5 line 35
X, Y	X: 1-7, 9-14, 16-20 Y: 14	GB 2318798 A	(HEWLETT-PACKARD) see abstract, page 5 line 3 to page 9 line 5
X	1-12, 17, 21, 22	GB 2252335 A	(ICI) see abstract, pages 1-3 especially
X, Y	X: 1, 2, 4, 7, 8, 13 at least Y: 14	US 4969951 A	(CANON) see abstract, col 1 line 45 to col 5 line 38
Y	14	JP 4183759 A	(SEIKO) and also WPI Abstract Acc. No. 1992-265689

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^v:

C4A

Worldwide search of patent documents classified in the following areas of the IPC⁷:

C09D

The following online and other databases have been used in the preparation of this search report:

WPI, EPODOC, PAJ